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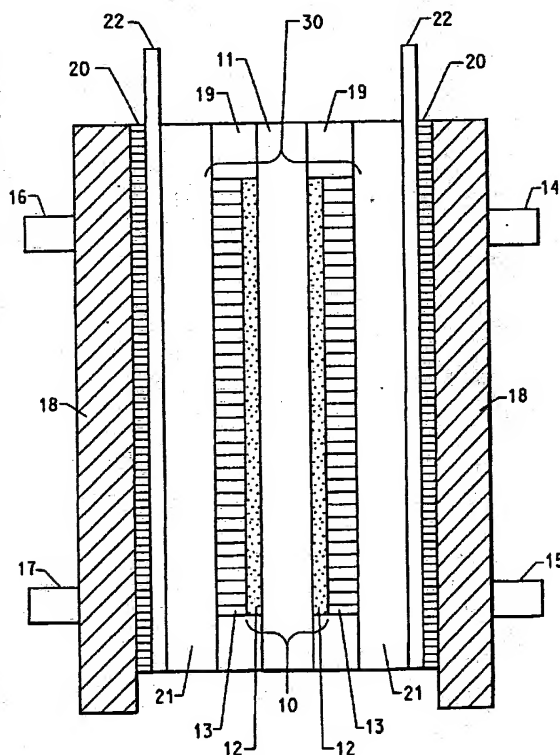
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(54) Title: PROCESS TO PREPARE STABLE TRIFLUOROSTYRENE CONTAINING COMPOUNDS GRAFTED TO BASE POLYMERS USING A SOLVENT/WATER MIXTURE



(57) Abstract: A fluorinated ion exchange polymer is prepared by grafting at least one grafting monomer derived from trifluorostyrene on to at least one base polymer in a organic solvent/water mixture. These ion exchange polymers are useful in preparing catalyst coated membranes and membrane electrode assemblies used in fuel cells.

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TITLE

PROCESS TO PREPARE STABLE TRIFLUOROSTYRENE CONTAINING
COMPOUNDS GRAFTED TO BASE POLYMERS USING A
SOLVENT/WATER MIXTURE

5

FIELD OF THE INVENTION

The present invention relates to a novel compound grafted to a
base polymer, and its use in electrochemical cells as membranes, and
more particularly to the use of these grafted polymers in fuel cells. This
invention was made with government support under Contract No. DE-
10 FC04-02AL67606 awarded by the U.S. Department of Energy. The
government has certain rights in the invention.

BACKGROUND OF THE INVENTION

Electrochemical cells, such as fuel cells and lithium-ion batteries
are known. Depending on the operating conditions, each type of cell
15 places a particular set of requirements upon the electrolytes used in them.
For fuel cells, this is typically dictated by the type of fuel, such as hydrogen
or methanol, used to power the cell and the composition of the membrane
used to separate the electrodes. Proton-exchange membrane fuel cells,
powered by hydrogen as the fuel, could be run at higher operating
20 temperatures than currently employed to take advantage of lower purity
feed streams, improved electrode kinetics, better heat transfer from the
fuel cell stack to improve its cooling. Waste heat is also employed in a
useful fashion. However, if current fuel cells are to be operated at greater
than 100 °C then they must be pressurized to maintain adequate hydration
25 of typical proton-exchange membranes to support useful levels of proton
conductivity.

There is an ongoing need to discover novel grafted films that
improve the performance of the latest generation of electrochemical cells,
such as fuel cells and lithium-ion batteries, to develop new membrane
30 materials that will maintain adequate proton conductivity at lower levels of
hydration and have sufficient durability for the intended application.

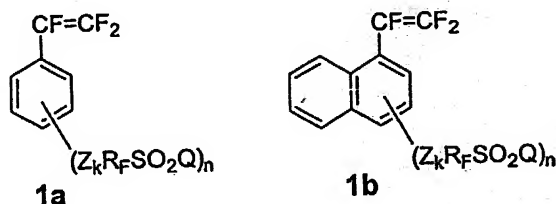
SUMMARY OF THE INVENTION

In a first aspect, the invention provides a grafting process for
making a fluorinated ion exchange polymer membrane comprising:

- (a) forming a monomer composition comprising at least one grafting monomer, in a mixture of water and one or more organic solvent;

wherein the grafting monomer comprises one or more of 1a or 1b:

5



- wherein Z comprises O, S, SO_2 , or POR wherein R comprises a linear or branched perfluoroalkyl group of 1 to 14 carbon atoms optionally containing oxygen or chlorine, an alkyl group of 1 to 8 carbon atoms, an aryl group of 6 to 12 carbon atoms or a substituted aryl group of 6 to 12 carbon atoms;

R_F comprises a linear or branched perfluoroalkylene group of 1 to 20 carbon atoms, optionally containing oxygen, sulfur or chlorine;

- Q is chosen from F, -OM, $-\text{NH}_2$, $-\text{N}(\text{M})\text{SO}_2\text{R}^2_\text{F}$, and $-\text{C}(\text{M})(\text{SO}_2\text{R}^2_\text{F})_2$, wherein M comprises H, an alkali cation, or ammonium;

R^2_F groups comprise alkyl of 1 to 14 carbon atoms which may optionally include ether oxygens or aryl of 6 to 12 carbon atoms where the alkyl or aryl groups may be perfluorinated or partially fluorinated;

- and k is 0 or 1, n is 1 or 2 for 1a, and n is 1, 2, or 3 for 1b;

- (b) irradiating at least one base polymer with ionizing radiation, and
- (c) contacting at least one base polymer with the monomer composition from step (a), at a temperature of about 0 °C to about 120 °C for about 0.1 hours to about 500 hours.

A second aspect of the invention is a polymer made by the process described above.

A third aspect of the invention is a catalyst coated membrane comprising a polymer electrolyte membrane having a first surface and a

second surface, wherein the polymer electrolyte membrane comprises the polymer described above.

A fourth aspect of the invention is a membrane electrode assembly comprising a polymer electrolyte membrane, having a first surface and a second surface, wherein the polymer electrolyte membrane comprises the polymer described above.

A fifth aspect of the invention is an electrochemical cell comprising a membrane electrode assembly, wherein the membrane electrode assembly comprises a polymer electrolyte membrane, having a first surface and a second surface, wherein the polymer electrolyte membrane comprises the polymer described above. The electrochemical cell can be a fuel cell.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is a schematic illustration of a single cell assembly.

DETAILED DESCRIPTION OF THE INVENTION

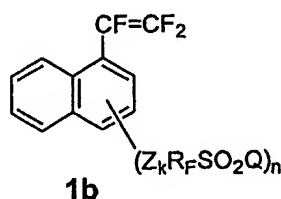
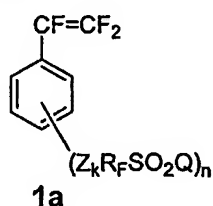
Fluorinated Ion Exchange Polymer:

The fluorinated ion exchange polymers of the invention are useful as polymer electrolyte membranes in fuel cells, chloralkali cells, batteries, electrolysis cells, ion exchange membranes, sensors, electrochemical capacitors, and modified electrodes.

Processes for making grafted polymers and membranes:

The invention is directed to a grafting process for making a fluorinated ion exchange polymer membrane comprising the steps of:

- (a) forming a monomer composition comprising at least one grafting monomer, in a mixture of water and one or more organic solvent; wherein the grafting monomer comprises one or more of 1a or 1b:



wherein Z comprises O, S, SO₂, or POR wherein R comprises a linear or branched perfluoroalkyl group of 1 to 14 carbon atoms optionally containing oxygen or chlorine, an alkyl group of 1 to 8 carbon atoms, an aryl group of 6 to 12 carbon atoms or a substituted aryl group of 6 to 12 carbon atoms;

R_F comprises a linear or branched perfluoroalkylene group of 1 to 20 carbon atoms, optionally containing oxygen, sulfur or chlorine;

Q is chosen from F, -OM, -NH₂, -N(M)SO₂R²_F, and -C(M)(SO₂R²_F)₂, wherein M comprises H, an alkali cation, or ammonium;

R²_F groups comprise alkyl of 1 to 14 carbon atoms which may optionally include ether oxygens or aryl of 6 to 12 carbon atoms where the alkyl or aryl groups may be perfluorinated or partially fluorinated;

and k is 0 or 1, n is 1 or 2 for 1a, and n is 1, 2, or 3 for 1b;

(b) irradiating at least one base polymer with ionizing radiation, and

(c) contacting at least one base polymer with the monomer composition from step (a), at a temperature of about 0 °C to about 120 °C for about 0.1 hours to about 500 hours.

The attached pendant group(s) in Formulae 1, 2, 1b and 2b can be attached to any open valence in the ring. In Formulae 1b and 2b the pendant group can be attached to either ring in the structure, and if more than one pendant group is present, can be attached to one or both rings.

As used herein, organic solvent is defined to mean an organic solvent that is miscible or at least partially soluble with water, and in which the monomer is at least partially soluble, but not including alcohols or glycols. Typical solvents include acetonitrile, dimethylformamide (DMF), dimethylacetamide (DMAC), dimethylsulfoxide (DMSO), and glycol ethers of the formula R(OCH₂CH₂)_pOR, wherein R is an alkyl group and p is 1 to 12. In different embodiments of the invention, the water content, on a weight basis, of the water plus organic solvent mixture (water/{water + organic solvent}) is the range of 10% to 99.99%, and preferably in the range of 40% to 90%.

The mixture of water and organic solvent can optionally contain one or more surfactants. The surfactant can be anionic, cationic, or nonionic, and can be fluorinated. Suitable surfactants include, are not limited to, sodium dodecylsulfate, alkyl benzene sulfonates, dextrans, alkyl-ether sulfonates, ammonium sulfates, Triton® surfactants, and fluorinated surfactants such as C8 (ammonium perfluorooctanoate) Zonyl® fluorosurfactants such as Zonyl® 62, Zonyl® TBS, Zonyl® FSP, Zonyl® FS-62, Zonyl® FSA, Zonyl® FSH, and fluorinated alkyl ammonium salts such as but not limited to $R'_wNH_{(4-w)}X$ wherein X is Cl^- , Br^- , I^- , F^- , HSO_4^- , or $H_2PO_4^-$, where R' is $(R_FCH_2CH_2)-$. Zonyl® fluorosurfactants are available from E. I. DuPont de Nemours, Wilmington, DE, and in general are anionic, cationic, amphoteric or nonionic oligomeric hydrocarbons containing ether linkages and fluorinated substituents. For example, Zonyl® FSP is an anionic surfactant of the formula $(R_FCH_2CH_2)_xPO(O^-NH_4^+)_y$, where $x + y = 3$ and Zonyl® FSH is a nonionic surfactant of the formula $R_FCH_2CH_2O(CH_2CH_2O)_wH$.

Enhancing additives can optionally be used to enhance the grafting rate or to enhance film quality. Suitable additives are water insoluble organic compounds that are solvents for the monomer or monomers used. One or more enhancing additives may be used. The enhancing additive is typically present at an amount of 0.5 to 300-weight % of the monomer. Suitable enhancing additives can include α,α,α -trifluorotoluene, dichlorobenzotrifluoride, chlorobenzotrifluoride, chlorobenzene, dichlorobenzene, trichlorobenzene, fluorobenzene, difluorobenzene, trifluorobenzene, perfluorobenzene, toluene, p-xylene, m-xylene, o-xylene, or C5-C10 aliphatic hydrocarbon, fluorohydrocarbon, fluorocarbon, and fluoroether.

In different embodiments of the invention, Q is F, R_F is chosen from $(CF_2)_q$ wherein $q=1$ to 16, $(CF_2)_qOCF_2CF_2$ wherein $q = 1$ to 12, and $(CF_2CF(CF_3)O)_qCF_2CF_2$ where q is 1 to 6, and R_F^2 is chosen from

methyl, ethyl, propyl, butyl, and phenyl, each of which may be partially fluorinated or perfluorinated, or R_F is chosen from $(CF_2)_q$ wherein $q=1$ to 4, $(CF_2)_qOCF_2CF_2$ wherein $q = 1$ to 4, and $(CF_2CF(CF_3)O)_qCF_2CF_2$ where q is 1 to 2. R_F^2 can be chosen from

5 perfluoromethyl, perfluoroethyl, and perfluorophenyl.

In the above process steps (b) and (c) can be performed simultaneously or sequentially.

The monomers can be obtained commercially or prepared using any process known in the art. Methods to prepare these monomers are

10 detailed in WO2005/113621, WO2005/049204, WO2005/113491, and WO2005/003083, all herein incorporated entirely by reference.

Base Polymer:

The base polymer to be used as the substrate for the grafting reaction may be a homopolymer or copolymer of non-fluorinated,

15 fluorinated, and perfluorinated monomers. Partially or completely fluorinated polymers often impart increased chemical stability and are more typical. The base polymer is typically chosen so that it imparts desirable mechanical properties to the final grafted polymer, is stable to the irradiation used to activate the polymer for grafting, and is stable under

20 the conditions to which it is exposed during use. For separators or membranes it is desirable that the base polymer be present in the form of a film, though other shapes may be desired depending on the electrochemical use. Some typical base polymers may include poly(ethylene-tetrafluoroethylene-termonomer) (ETFE) that comprises a

25 terpolymer of ethylene and tetrafluoroethylene (TFE), in the range of 35:65 to 65:35 (mole ratios) with from 1 to 10 mole% of a termonomer, perfluorobutyl ethylene in the case of DuPont Tefzel®; ETFE copolymers also using other termonomers (Neoflon® ETFE); ECTFE that comprises a copolymer of ethylene and chlorotrifluoroethylene; FEP that comprises a

30 copolymer of TFE and hexafluoropropylene (HFP), optionally containing a minor amount (1-3 mol%) of perfluoro(alkyl vinyl ether) (PAVE), usually perfluoro(propyl vinyl ether) (PPVE) or perfluoro(ethyl vinyl ether) (PEVE);

PFA that comprises a copolymer of TFE and PAVE, wherein PAVE may be PPVE or PEVE; MFA that comprises a copolymer of TFE, PMVE, and PPVE; PTFE that comprises a homopolymer of TFE; modified PTFE, that contains up to 0.5 mol% of another monomer, usually a PAVE; PVF that
5 comprises a polymer of vinyl fluoride (VF); PVDF that comprises a polymer of vinylidene fluoride (VF₂); copolymers of VF₂ and HFP which are sold under the trademarks KynarFlex® and Viton® A by Atofina and by DuPont, respectively; polyethylene and polypropylene. The term "modified" distinguishes these polymers from copolymers of TFE. The
10 modified PTFE polymers are, like PTFE, not melt processible.

Typically, the base polymer may be chosen from poly(ethylene-tetrafluoroethylene), poly(ethylene-tetrafluoroethylene-termonomer) (Tefzel®, Neoflon® ETFE); poly(tetrafluoroethylene-hexafluoropropylene) (Teflon® FEP); poly(tetrafluoroethylene-perfluorovinylether) (Teflon®
15 PFA), polytetrafluoroethylene (Teflon® PTFE); poly(ethylene-chlorotrifluoroethylene); poly(vinylidene fluoride) (Kynar® or Solef®); and poly(vinylidene fluoride-hexafluoropropylene) (Kynar® Flex). More typically, the base polymer is chosen from poly(ethylene-tetrafluoroethylene-termonomer), poly(tetrafluoroethylene-hexafluoropropylene), poly(tetrafluoroethylene-perfluoropropylvinylether),
20 and poly(vinylidene fluoride).

Free radicals may be created in the base polymer in order to produce attachment sites for the grafting monomers using radiation. When the base polymer is in film form, the films are known as irradiated
25 films. The radiation dosage should be sufficient to allow for the desired graft level to be reached, but not so high as to cause excessive radiation damage. Graft level is defined as (wt. of grafted polymer – wt. of base polymer)/(wt. of base polymer). (This is also known as weight uptake). The ionizing radiation may be provided in the form of electron beam,
30 gamma ray, or X-rays. Electron beam irradiation is typically performed at a high dose rate that may be advantageous for commercial production. The irradiation may be done while the base polymer is in contact with the grafting monomers (simultaneous irradiation and grafting). However, if the

free radicals of the base polymer are sufficiently stable, then the irradiation may be performed first and in a subsequent step the base polymer may be brought into contact with the grafting monomers (post-irradiation grafting). Base polymers suitable for the post-irradiation grafting method are usually

5 fluorinated polymers. In this case the irradiation may typically be done at sub-ambient temperatures, for example with base polymer cooled with dry ice, and it may be stored at a sufficiently low temperature to prevent decay of the free radicals prior to its use in the grafting reaction.

With some substrates, such as poly(ethylene-tetrafluoroethylene)

10 the irradiation may be performed in the presence of oxygen or in an oxygen-free environment, and an appreciable graft level can be obtained in either case. Typically grafting may be performed in an inert gas, such as nitrogen or argon. This may be accomplished by loading the base polymer films, within an inert-atmosphere box, into oxygen-barrier bags,

15 sealing them shut (with or without grafting monomers and solvent), and then irradiating. In the case of post-irradiation grafting, the base polymer may then also be stored in the oxygen-free environment before and during the grafting reaction.

The grafting reaction may be performed by exposing the base

20 polymer to a monomer composition containing the grafting monomers. It is generally desirable to lower the quantity of fluorinated monomer used in the grafting reaction, and this may be accomplished by diluting it by forming a mixture with water and organic solvent, which thus increases the total working volume of the monomer composition. The monomer

25 composition may thus be an emulsion made by mechanical or ultrasonic mixing of the monomers with water, the organic solvent, and optional surfactants. The monomer may also be additionally present in a separate phase and only partially soluble in the mixture of water and organic solvent..

30 Grafting may be accomplished by contacting the base polymer films, during irradiation or subsequent to irradiation, with the monomer composition and holding films at about 0 °C to about 120 °C for about 0.1 to about 500 hours. Typical temperatures are about 25 °C to about 100

°C, more typically about 35 to about 90 °C, and most typically about 40 to about 80 °C. Typical times are about 10 min to about 300 hours, more typically about 1 hour to about 200 hours, and most typically about 1 hour to about 100 hours.

- 5 Subsequent to the grafting reaction, the emulsion, additive if present and unreacted monomer may be removed by extraction with a low-boiling solvent or through vaporization. The grafted polymer may also be extracted with a solvent in order to remove any polymer formed in the film that is not grafted to the base film.

10 Preparation of Ionic Polymers:

- This invention provides for the facile conversion of the fluorosulfonyl fluorides to acid form, without the use of sulfonation reagents. Polymers grafted with the monomers bearing pendant sulfonyl fluoride groups may be hydrolyzed with bases such as MOH or M_2CO_3 ($M = Li, Na, K, Cs,$
15 NH_4) or MOH in MeOH and/or DMSO, and water. The hydrolysis may usually be carried out at room temperature to about 100°C, typically at room temperature to about 80°C. With polymeric substrates such as PVDF that are sensitive to strong base, it is preferable to use the weaker carbonate bases that avoid decomposition of the substrate. Treatment of
20 polymeric salts with acids such as HNO_3 gives polymeric acids.

 The grafted sulfide polymers ($Z = S$) may be oxidized to sulfone polymers ($Z = SO_2$) using CrO_3 or hydrogen peroxide.

Electrochemical Cell:

- As shown in Figure 1, an electrochemical cell, such as a fuel cell,
25 comprises a catalyst-coated membrane (CCM) (10) in combination with at least one gas diffusion backing (GDB) (13) to form an unconsolidated membrane electrode assembly (MEA). The catalyst-coated membrane (10) comprises a polymer electrolyte membrane (11) discussed above and catalyst layers or electrodes (12) formed from an electrocatalyst coating
30 composition. The fuel cell may be further provided with an inlet (14) for fuel, such as hydrogen; liquid or gaseous alcohols, e.g. methanol and ethanol; or ethers, e.g. diethyl ether, etc., an anode outlet (15), a cathode gas inlet (16), a cathode gas outlet (17), aluminum end blocks (18) tied

together with tie rods (not shown), a gasket for sealing (19), an electrically insulating layer (20), graphite or metal current collector blocks with flow fields for gas distribution (21), and gold plated current collectors (22).

Alternately, gas diffusion electrodes comprising a gas diffusion backing having a layer of an electrocatalyst coating composition thereon may be brought into contact with a solid polymer electrolyte membrane to form the MEA.

The electrocatalyst coating compositions used to apply the catalyst layers as electrodes on the CCM (10) or the GDE comprise a combination of catalysts and binders dispersed in suitable solvents for the binders, and may include other materials to improve electrical conductivity, adhesion, and durability. The catalysts may be unsupported or supported, typically on carbon, and may differ in composition depending on their use as anodes or cathodes. The binders may consist of the same polymer used to form the polymer electrolyte membrane (11), but may contain in part or be solely composed of other suitable polymer electrolytes as needed to improve the operation of the fuel cell. Some examples include Nafion® perfluorosulfonic acid, sulfonated polyether sulfones.

The fuel cell utilizes a fuel source that may be in the gas or liquid phase, and may comprise hydrogen, an alcohol, or an ether. The fuel is humidified to the degree required to maintain adequate ionic conductivity in the solid polymer electrolyte membrane discussed above so that the fuel cell provides a high power output. Depending on the operating temperature, the fuel cell may be operated at elevated pressures to maintain the required degree of humidification. Typically a gaseous humidified hydrogen feed or methanol/water solution may be supplied to the anode compartment, and air or oxygen supplied to the cathode compartment.

Catalyst Coated Membrane:

A variety of techniques are known for CCM manufacture, which apply an electrocatalyst coating composition similar to that described above onto a solid polymer electrolyte membrane. Some known methods

include spraying, painting, patch coating and screen, decal, pad or flexographic printing.

In one embodiment of the invention, the MEA (30), shown in Figure 1, may be prepared by thermally consolidating the gas diffusion backing (GDB) with a CCM at a temperature of under about 200 °C, typically about 140 to about 160 °C. The CCM may be made of any type known in the art. In this embodiment, an MEA comprises a solid polymer electrolyte (SPE) membrane with a thin catalyst-binder layer disposed thereon. The catalyst may be supported (typically on carbon) or unsupported. In one method of preparation, a catalyst film is prepared as a decal by spreading the electrocatalyst coating composition on a flat release substrate such as Kapton® polyimide film (available from the DuPont Company). After the coating dries, the decal is transferred to the surface of the SPE membrane by the application of pressure and heat, followed by removal of the release substrate to form a catalyst coated membrane (CCM) with a catalyst layer having a controlled thickness and catalyst distribution. Alternatively, the catalyst layer is applied directly to the membrane, such as by printing, and the catalyst film is then dried at a temperature not greater than about 200 °C.

The CCM, thus formed, is then combined with a GDB to form the MEA (30). The MEA is formed, by layering the CCM and the GDB, followed by consolidating the entire structure in a single step by heating to a temperature no greater than about 200 °C, typically in the range of about 140 to about 160 °C, and applying pressure. Both sides of the MEA can be formed in the same manner and simultaneously. Also, the composition of the catalyst layer and GDB may be different on opposite sides of the membrane.

The invention is illustrated in the following examples.

EXAMPLES

30 Example 1: Irradiated Films

ETFE films were obtained in thicknesses of 30 µm and 55 µm (Tefzel® LZ5100 and LZ5200, DuPont Company, Wilmington, DE). PVdF films were obtained with a thickness 50 µm (Kynar® Goodfellow Corp,

Berwyn, PA). The films were degassed and brought into a nitrogen-filled glove box. They were cut to size and sealed inside gas-barrier bags (PPD aluminum-foil-barrier bags from Shield Pack, Inc., West Monroe, LA). Dry ice pellets were placed in a metal tray for cooling and the bags with films
5 were placed into the metal tray. The films were irradiated using an electron beam accelerator using 1 MV and a current of 2.2 mA or 4.5 MV and 25 mA. Up to 6 films were placed in each bag, and the bags were stacked up to 2 high in the tray. The beam was electronically scanned across a 40" aperture while the metal tray was moved slowly beneath the
10 beam. Each pass resulted in a dosage of 20 kGy, and from 1 to 13 passes were used resulting in total dosages between 20 and 260 kGy. For dosages above 190 kGy, the passes were broken in to two groups with the inclusion of a three-minute pause between the groups to allow the bags to cool. The irradiated films were stored in the bags under dry ice or
15 in a refrigerator cooled to -40 °C.

Example 2

Tefzel® films from Example 1 of 27 µm thickness and irradiated to 140 kGy were brought into a nitrogen-purged glove box, cut to 35 mm X 35 mm size, and weighed. Into each of three wide-mouth jars (66 mm ID
20 X 70 mm high) was placed 0.50 g of deoxygenated monomer $p\text{-CF}_2=\text{CF}-\text{C}_6\text{H}_4-\text{S}(\text{CF}_2)_2\text{SO}_2\text{F}$, one film, solvent as indicated in the Table below, and water. A piece of Teflon® mesh was added to each jar to hold the film under the liquid, polymeric lids were attached to the jars, and the jars brought out of the glove box. The jars were placed in an incubator
25 shaker box (New Brunswick Scientific Co., Inc. Series 25) heated to 60 °C and gently shaken at 125 rpm for 96 hr. After this grafting reaction, the liquids were poured out of the jars and tetrahydrofuran (THF) was added to each bottle. The grafted films were extracted using the THF for 18 hr at ambient temperature, after which the films were removed, dried in ambient
30 air, and reweighed.

Sample	Solvent	Solvent wt (g)	Wt of water (g)	Graft Level (%)
A	acetone	6.5	3.5	25
B	tetrahydrofuran	6.5	3.5	11

Example 3

- A 30 mL bottle with a stirring bar was charged with a Tefezi[®] film
- 5 irradiated with 140 kGy dosage under nitrogen then water, solvent and monomers in amounts as listed below table were added into the bottle under N₂. The mixture was stirred in the sealed bottle at 60 °C for 3 days. The films were removed from the bottle water and dried in a vacuum oven at 60 °C with nitrogen bleed for 2 hrs to give the grafted film. Graft level
- 10 was calculated as $(w_g - w)/w$, where w is the initial weight of the film and w_g is the weight of the dried washed grafted film.

Example No.	CH ₃ CN (mL)	DMSO (ml)	H ₂ O (mL)	monomer (g)	GL% after drying
1	8		17	1	165
2	5		20	1	193
3	15		10	1	168
4	10		15	1	173
5		15	10	1	109
6		5	20	1	48

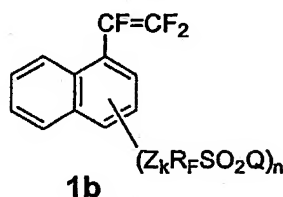
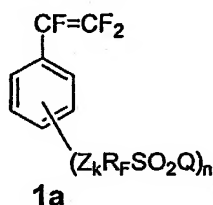
CLAIMS

What is claimed is:

1. A grafting process for making a fluorinated ion exchange polymer membrane comprising:

- 5 (a) forming an monomer composition comprising at least one grafting monomer, in a mixture of water and one or more organic solvent;

wherein the grafting monomer comprises one or more of 1a or 1b:



10

wherein Z comprises O, S, SO₂, or POR wherein R comprises a linear or branched perfluoroalkyl group of 1 to 14 carbon atoms optionally containing oxygen or chlorine, an alkyl group of 1 to 8 carbon atoms, an aryl group of 6 to 12 carbon atoms or a substituted aryl group of 6 to 12 carbon atoms;

15

R_F comprises a linear or branched perfluoroalkylene group of 1 to 20 carbon atoms, optionally containing oxygen, sulfur or chlorine;

Q is chosen from F, -OM, -NH₂, -N(M)SO₂R²_F, and -C(M)(SO₂R²_F)₂, wherein M comprises H, an alkali cation, or ammonium;

20

R²_F groups comprise alkyl of 1 to 14 carbon atoms which may optionally include ether oxygens or aryl of 6 to 12 carbon atoms where the alkyl or aryl groups may be perfluorinated or partially fluorinated;

and k is 0 or 1, n is 1 or 2 for 1a, and n is 1, 2, or 3 for 1b;

25

(b) irradiating at least one base polymer with ionizing radiation, and

(c) contacting at least one base polymer with the monomer composition from step (a), at a temperature of about 0 °C to about 120 °C for about 0.1 hours to about 500 hours.

2. The process of Claim 1 wherein the organic solvent is miscible or at least partially soluble with water, and wherein the monomer is partially soluble in the organic solvent.
3. The process of Claim 2 wherein the organic solvent is
5 acetonitrile, dimethylformamide, dimethylacetamide, dimethylsulfoxide, or glycol ethers of the formula $R(OCH_2CH_2)_pOR$, wherein R is an alkyl group and p is 1 to 12.
4. The process of Claim 1 wherein the weight % of water to the sum of water and organic solvent in the mixture is in the range of 10% to
10 99.99%.
5. The process of Claim 4 wherein the weight % of water to the sum of water and organic solvent in the mixture is in the range of 40% to 90%.
6. The process of Claim 1 wherein the organic solvent and water
15 mixture optionally includes an enhancing additive.
7. The process of Claim 6 wherein the enhancing additive is α,α,α -trifluorotoluene, dichlorobenzotrifluoride, chlorobenzotrifluoride, chlorobenzene, dichlorobenzene, trichlorobenzene, fluorobenzene, difluorobenzene, trifluorobenzene, perfluorobenzene, toluene, p-xylene, m-
20 xylene, o-xylene, or C5-C10 aliphatic hydrocarbon, fluorohydrocarbon, fluorocarbon, or fluoroether.
8. The process of Claim 4 wherein the enhancing additive is present at an amount of 0.5 to 300 weight % of the monomer.
9. The process of Claim 1 wherein the at least one base polymer
25 is in film form.
10. The process of Claim 1 wherein steps (b) and (c) are performed simultaneously.
11. The process of Claim 1 wherein steps (b) and (c) are performed sequentially.
- 30 12. The process of Claim 1 wherein Q comprises F.
13. The process of Claim 1 wherein R_F is chosen from $(CF_2)_q$ wherein $q=1$ to 16, $(CF_2)_qOCF_2CF_2$ wherein $q = 1$ to 12, and

$(\text{CF}_2\text{CF}(\text{CF}_3)\text{O})_q\text{CF}_2\text{CF}_2$ where q is 1 to 6, and R^2_{F} is chosen from methyl, ethyl, propyl, butyl, and phenyl, each of which may be partially fluorinated or perfluorinated.

14. The process of Claim 13 wherein R_{F} is chosen from
 5 $(\text{CF}_2)_q$ wherein $q=1$ to 4, $(\text{CF}_2)_q\text{OCF}_2\text{CF}_2$ wherein $q = 1$ to 4, and $(\text{CF}_2\text{CF}(\text{CF}_3)\text{O})_q\text{CF}_2\text{CF}_2$ where q is 1 to 2, and R^2_{F} is chosen from perfluoromethyl, perfluoroethyl, and perfluorophenyl.

15. The process of Claim 1 wherein the base polymer comprises a homopolymer or copolymer prepared from non-fluorinated, fluorinated, or
 10 perfluorinated monomers.

16. The process of Claim 15 wherein the base polymer is chosen from poly(ethylene-tetrafluoroethylene), poly(ethylene-chlorotrifluoroethylene), poly(tetrafluoroethylene-hexafluoropropylene), poly(tetrafluoroethylene-perfluoroalkyl vinyl ether),
 15 poly(tetrafluoroethylene-perfluoromethyl vinyl ether), poly(tetrafluoroethylene-perfluoropropyl vinyl ether), polytetrafluoroethylene, modified polytetrafluoroethylene, polyvinyl fluoride, polyvinylidene fluoride, poly(vinylidene fluoride-hexafluoropropylene), polyethylene, and polypropylene.

- 20 17. The process of Claim 15 wherein the base polymer comprises a partially or completely fluorinated polymer.

18. The process of Claim 17 wherein the base polymer is chosen from poly(ethylene-tetrafluoroethylene), poly(ethylene-tetrafluoroethylene-
 25 termonomer), poly(tetrafluoroethylene-hexafluoropropylene), poly(tetrafluoroethylene-perfluorovinylether), polytetrafluoroethylene, poly(ethylene-chlorotrifluoroethylene); poly(vinylidene fluoride), and poly(vinylidenefluoride-hexafluoropropylene).

19. A polymer made by the process of Claim 1.

20. A catalyst coated membrane comprising a polymer electrolyte
 30 membrane having a first surface and a second surface, wherein the polymer electrolyte membrane comprises the polymer of Claim 17.

21. A membrane electrode assembly comprising a polymer electrolyte membrane, having a first surface and a second surface, wherein the polymer electrolyte membrane comprises the polymer of Claim 17.
- 5 22. An electrochemical cell comprising a membrane electrode assembly, wherein the membrane electrode assembly comprises a polymer electrolyte membrane, having a first surface and a second surface, wherein the polymer electrolyte membrane comprises the polymer of Claim 17.
- 10 23. The electrochemical cell of Claim 22 wherein the electrochemical cell is a fuel cell.

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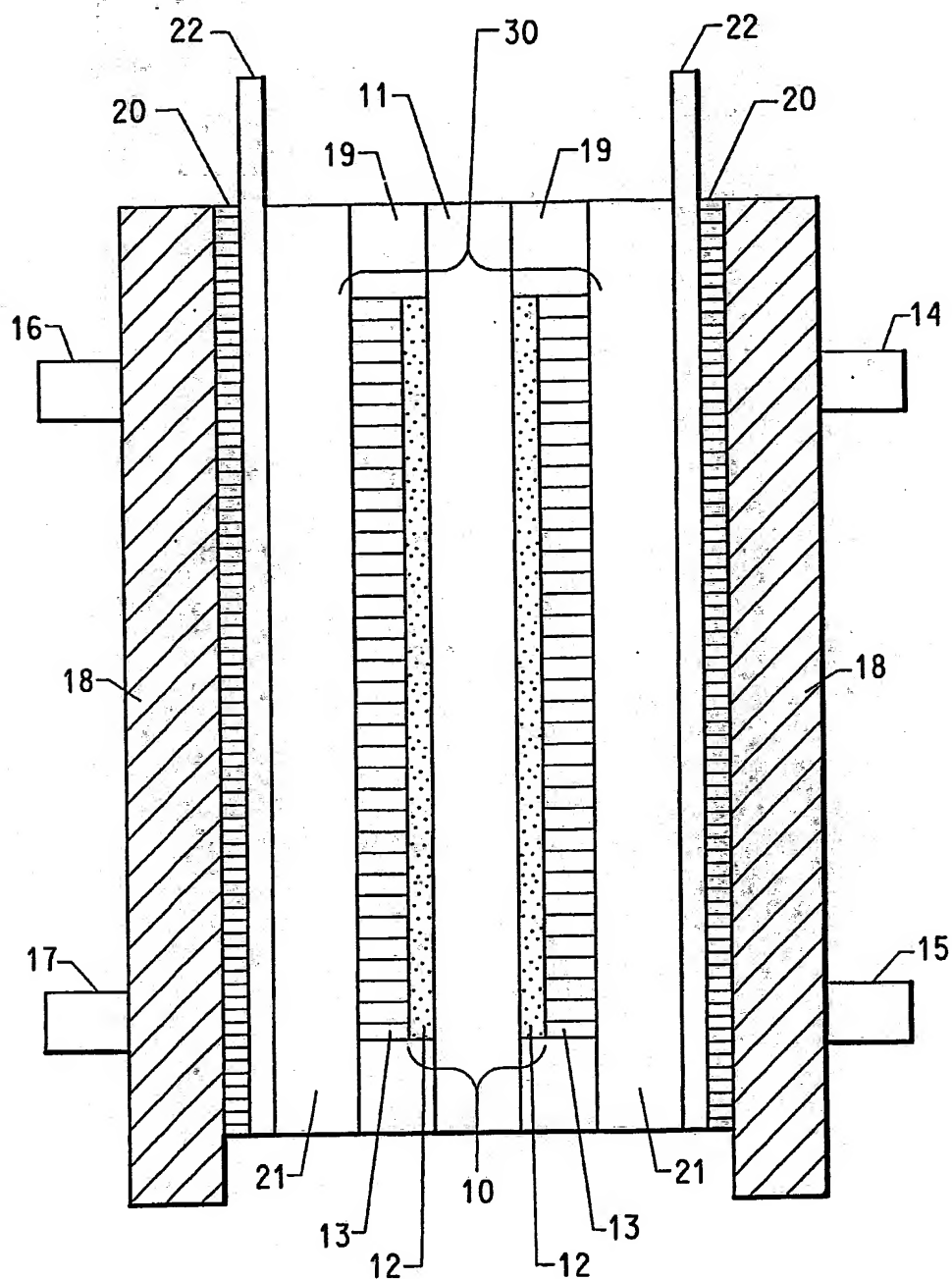


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2006/011179

A. CLASSIFICATION OF SUBJECT MATTER
 INV. B01D71/28 H01M8/10 B01D67/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F B01D H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X,P	WO 2005/049204 A (E.I. DUPONT DE NEMOURS AND COMPANY) 2 June 2005 (2005-06-02) cited in the application claims 1-72	1-23
X	WO 01/58576 A (BALLARD POWER SYSTEMS INC.) 16 August 2001 (2001-08-16) page 4, line 21 - page 9, line 26; claims 1-62	1-23
X	US 6 359 019 B1 (BALLARD POWER SYSTEMS INC.) 19 March 2002 (2002-03-19) column 2, line 25 - column 6, line 51; claims 1-39	1-23
A	WO 03/018654 A (BALLARD POWER SYSTEMS INC.) 6 March 2003 (2003-03-06) the whole document	1-23

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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